ploded in the oil bath used, and at higher temperatures this was even more of a problem. Since the reaction is highly exothermic and the compounds probably boil at near 100°, these small explosions probably resulted merely from the vapor pressures of samples rather hotter than the bath. Explosions of the solvent diluted samples used in kinetic work were not observed.

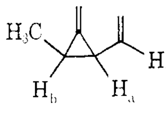
The proton spectra of C and E used for structural assignment were taken at 60 MHz in carbon disulfide at temperatures low enough to prevent rearrangement. The spectra were very noisy and did not show all details, but the following features allowed an assignment.

(1) E and C both showed olefinic absorption essentially identical with that of the parent compound[3] within the available precision. This allows the methyl substituent to be only at the 3 position.

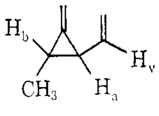
(2) In the saturated region E showed a somewhat broad single peak at δ 1.2, and a weaker doublet ($J \sim 9$ Hz, δ 1.64).

(3) In the saturated region C showed a doublet ($J \sim 6$ Hz, δ 1.07) with the low-field component 1.8 times as strong as the high field one. The doubly allylic proton must have been broader or more split than in E, or it would have been visible over the noise level.

We assign structures and peaks as follows using the notation illustrated.



C



E

In C the methyl group (δ 1.07) is coupled to H_b, and using the AB_3 models from Wiberg and Nist,[16] we deduce that H_b should center at roughly δ 1.50, but the coupling with H_a and with the methyl protons keeps it invisible. Similarly H_a is invisible because of two large couplings with H_b and H_v.

In E, the methyl group signal is largely in the single peak at δ 1.2, implying that for H_b δ is rather close to this value. H_b is itself not visible, presumably it is too highly split. Again using the Wiberg and Nist models we conclude that for H_b $\delta \leq 1.38$. H_a is visible and lies at δ 1.64 showing only one large coupling, presumably with H_v. The coupling to H_b is apparently much smaller, as is usually the case in *trans*-cyclopropyl protons.[17]

The stereochemical assignment is based on several factors. First, E, relative to the parent compound, is missing a large coupling in H_a, hence the H_b is trans to H_a. Second, the invisible H_b absorbs at smaller δ in E than in C, and in the parent the small δ signal is associated with the proton cis to the vinyl group. Third, the methyl protons in C are more shielded than those in E, consistent with a position cis to the vinyl group.

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(16) K. B. Wiberg and B. J. Nist, "The Interpretation of NMR Spectra," W. A. Benjamin, New York, N. Y., 1962, p 303.

(17) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Oxford, 1969, p 286.

Photobenzidine Rearrangements. III. The Photochemistry of 1,4-Diaryl-1,4-dimethyl-2-tetrazenes[1,2]

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Abstract: The photodecomposition of a series of 1,4-diaryl-1,4-dimethyl-2-tetrazenes in solution has been shown to produce the corresponding *N,N'*-dimethylhydrazoaryls as the major photoproducts. The quantum yields for photodecomposition with various aryl substituents were found to be (methanol solution): *p*-CO_2Et, 0.41; *p*-Cl, 0.21; *p*-H, 0.21; *p*-CH_3, 0.16; *p*-OEt, 0.08. A similar trend was found for quantum yields of decomposition in cyclohexane. The tetrazenes have been found to fluoresce at 77°K in ethanol and their fluorescence quantum yields were measured: *p*-CO_2Et, 0.6; *p*-Cl, 0.3; *p*-H, 0.1; *p*-CH_3, 0.1; *p*-OEt, 0.04. Sensitization experiments with acetone and phenanthrene and quenching experiments with oxygen and piperylene indicate a singlet state reaction. It is concluded that the variations in quantum yields of decomposition at 25° and of fluorescence at low temperature reflect the effect that substituents have on intersystem crossing to a nonreactive triplet state.

In an earlier publication we illustrated the connection between the photochemistry of 1,4-dimethyl-1,4-diphenyl-2-tetrazene (**1a**) and *N,N'*-dimethylhydrazobenzene (**2a**).[4] It was shown that **2a** rearranged to the *p*-semidine (**3**) when irradiated in hexane solution, and that, when similarly irradiated, **1a** gave **2a** in good yield accompanied by *N*-methylaniline and some of **3**. Subsequently, it was shown that the photorearrangement of some other *N,N'*-dimethylhydrazobenzenes occurred quite easily.[2] We have turned our attention now to analogous 1,4-dimethyl-1,4-diaryl-2-tetrazenes in order to learn more about their photodecomposition.

Few reports on the photochemistry of 2-tetrazenes are to be found in the literature. A number of 1,4-dialkyl-1,4-diphenyl-2-tetrazenes (dimethyl, diethyl, dipropyl, dibutyl) were reported by Child and coworkers to undergo photodecomposition,[5] among which **1a** gave **2a** and *N*-methylaniline (**4a**). Imoto's group has found that **1a** is moderately active in photoinitiating the polymerization of styrene and other monomers.[6] The formation of *o*- and *p*-chloroacetanilide from photolyzing 1,4-diacetyl-1,4-diphenyl-2-tetrazene in solutions of chlorine atom donors has been interpreted as involving the photodecomposition of the tetrazene.[7] In none of these reports is detailed information given on the way in which light initiates the decomposition of tetrazenes, except for the deduction[6,7]

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(1) Supported by Grant No. D-028 from the Robert A. Welch Foundation.

(2) Part II: H. J. Shine and J. D. Cheng, *J. Org. Chem.*, **36**, 2787 (1971).

(3) Postdoctoral Fellow.

(4) J. F. Sullivan, K. Hailey, and H. J. Shine, *Tetrahedron Lett.*, 2007 (1970).

(5) R. G. Child, G. Morton, C. Pidacks, and A. S. Tomcufcik, *Nature* (*London*), 391 (1964).

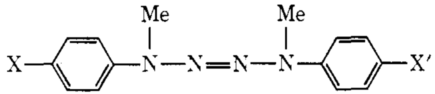
(6) K. Sugiyama, T. Nakaya, and M. Imoto, *J. Polym. Sci., Part A*, **10**, 205 (1972).

(7) K. M. Johnston, G. H. Williams, and H. J. Williams, *Chem. Ind.* (*London*), 991 (1966).

that substituted amino radicals are formed. A particularly complete case for deducing that diarylamino radicals are formed has been presented by Bridger in the comparison of the photodecomposition and thermal decomposition of 1,4-di(2-naphthyl)-1,4-diphenyl-2-tetrazene with the oxidation of *N*-phenyl-2-naphthylamine.[8]

Nelsen and coworkers have shown with esr data that in the photodecomposition of 1,4-diaryl-1,4-di-*tert*-butyl-2-tetrazenes radicals of the type ArṄR (R = *tert*-butyl) are formed and are members of Walter's "class S" radicals.[9]

We have now studied the photodecomposition and fluorescence spectroscopy of the series **1a–f**, and are able to provide further insight to the factors which control photodecomposition of these tetrazenes.



1

	a	b	c	d	e	f
X	H	OEt	Me	Cl	Me	CO_2Et
X'	H	OEt	Me	Cl	CO_2Et	CO_2Et

Results

Products. The tetrazenes **1a–f** have two maxima in their absorption spectra, one in the region of 240–250 nm and the other (larger) in the region of 340–380 nm. Irradiation of solutions of the tetrazenes at the second maximum causes clean decomposition, principally into the corresponding *N,N'*-dimethylhydrazobenzenes. When irradiation is carried out with a monochromator, the decomposition of a tetrazene can be followed spectroscopically (as explained in the Experimental Section). The maximum in the region of 340–380 nm decreases while others form in the regions of 240–250 and 300 nm until finally the spectrum has the characteristic bands of an *N*-methylarylamine chromophore. The change goes through isosbestic points in each case (in contrast with our earlier report[4]). An example is given with **1b** in Figure 1. Two other products are obtainable from irradiation of each tetrazene. One is the scission amine (an *N*-methylaniline), and the other a rearrangement product (the *p*-semidine from **1a** and an *o*-semidine from each of **1b–f**). However, these were isolated only in the case of **1a**.

Control experiments showed that **2a** is photostable under conditions where the *p*-semidine (**3**) and *N*-methylaniline (**4**) as well as **2a** are observable by tlc as photoproducts of **1a**.

It was reported earlier that **2a**, **2c**, and **2d** were isolated by tlc and assayed spectroscopically in yields of 67–75%.[4] Continued work in isolating hydrazo compounds has given the results in Table I.

Quantum Yields of Disappearance and Fluorescence of 1a–f. Quantum yields (Φ_d) for the disappearance of **1a–f** under irradiation in the region 340–380 nm are given in Table II. A clear substituent effect is shown in that the more electron donating is the substituent, the lower is the yield. Attempts were made to separate products of low conversion by tlc and so determine the quantum yields of product formation. Trial experiments showed, however, that the losses in removing small amounts of materials from plates were considerable and variable, and, therefore, the attempts were abandoned.

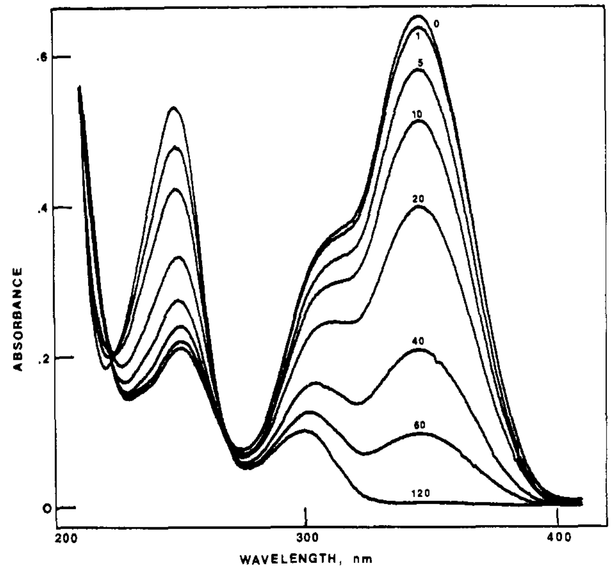


Figure 1. Changes in the absorption spectrum of 1,4-dimethyl-1,4-di-*p*-tolyl-2-tetrazene (**1c**) in cyclohexane solution. $[\mathbf{1c}]_0$ was 2.8×10^{-5} *M*. The set of traces represents decreasing absorbance at 345 nm and increasing absorbance at 247 nm, which occurred by irradiating the solution with 345-nm light in a monochromator (see Experimental Section). The traces were made after 0, 1, 5, 10, 20, 40, 60, and 120 cumulative min of irradiation at room temperature.

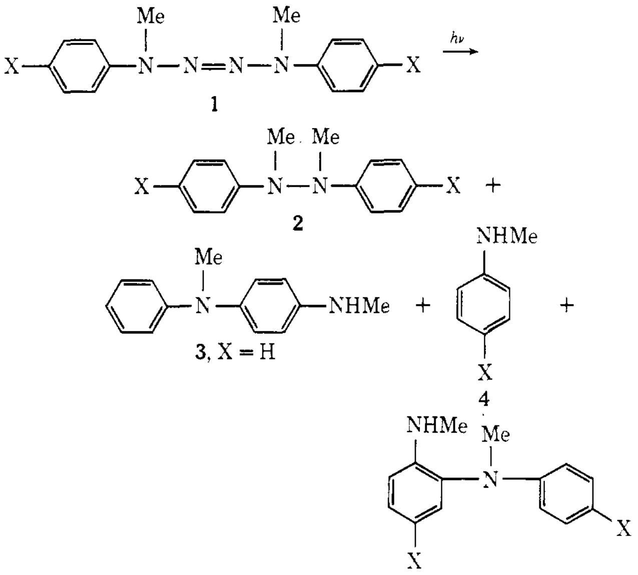


Table I. Products (**2**) from Preparative Scale Irradiations of Tetrazenes (**1**)

Tetrazene (**1**)	Hydrazo compd (**2**), %
a	43[4]
c	83
d	57
f	83

The tetrazenes **1a–f** fluoresce in solution at low but not at room temperature. No evidence of phosphorescence was obtained. The observed luminescence

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(8) R. F. Bridger, *J. Amer. Chem. Soc.*, **94**, 3124 (1972).

(9) S. F. Nelsen, R. T. Landis, L. H. Kiehle, and T. H. Leung, *J. Amer. Chem. Soc.*, **94**, 1610 (1972).

Table II. Quantum Yields (Φ_d) for the Decomposition of Tetrazenes **1a–f** at 25°

Compd	Substituent p	p'	λ_{max}	Φ_d(cyclohexane)	Φ_d(methanol)
b	OEt	OEt	347	0.15	0.08
c	Me	Me	344	0.35	0.16
a	H	H	343	0.36	0.21
d	Cl	Cl	349	0.41	0.21
e	Me	CO_2Et	363	0.43	
f	CO_2Et	CO_2Et	377	*a*	0.41

[a] Compound not sufficiently soluble for determination.

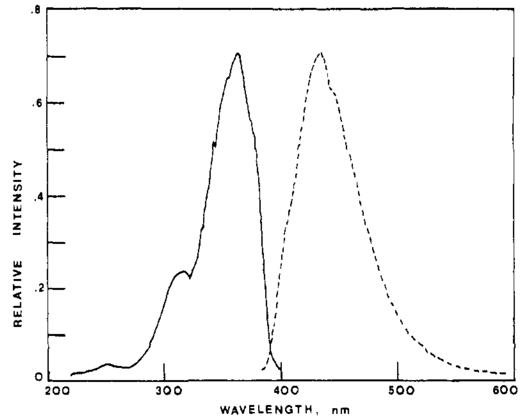

Figure 2. Spectra of 3.4×10^{-5} *M* 1,4-dimethyl-1,4-di-*p*-tolyl-2-tetrazene (**1c**) in absolute ethanol at 77°K: (—) excitation with λ_{em} 431 nm; (- - - - -) emission with λ_{ex} 363 nm.

is diagnosed as fluorescence from the overlap of excitation and emission bands in the 0–0 band region and from the short luminescence lifetimes which allowed complete suppression of the emission when the phosphoroscope was used. Fluorescence quantum yields (Φ_f) were determined and are given in Table III. The yields were obtained by comparison with anthracene as a standard.[10] They are not precise since corrections for the response of the phototube to various emission maxima were not made. Listed in Table III is also the approximate 0–0 luminescence band for each compound, estimated from the region of overlap of the excitation and emission bands of the compound (*e.g.*, as in Figure 2). Table III shows that the effect of para substituents on Φ_f parallels that on Φ_d.

Table III. Fluorescence Quantum Yields (Φ_f) of Tetrazenes **1a–f** at 77°K in Absolute Ethanol[a]

Compd and para substituent	λ_{max}, nm emission	0–0 band, nm	Φ_f
1b, OEt	457	400	0.04
1c, Me	431	390	0.1
1a, H	424	385	0.1
1d, Cl	421	388	0.3
1f, CO_2Et	410, 434	403	0.6

[a] The exciting wavelength was 350 nm in all cases.

Sensitizing and Quenching Experiments. Experiments were carried out with **1a**. Photodecomposition was not enhanced by using acetone as solvent, was not sensitive to the presence of dissolved oxygen, and was not quenched in the presence of 0.05 and 0.10 *M* piperylene (Table IV). On the other hand, photodecomposition was sensitized by the singlet-sensitizer phenanthrene (λ_{max} 270 nm),[11] and the sensitized decomposition was not affected by adding the triplet-quencher piperylene. Relevant quantum yields are given in Table V.

Table IV. Quantum Yields (Φ_d) for the Decomposition of **1a** in the Presence of Piperylene at 25° [a]

[**1a**], $M \times 10^5$	[Piperylene], *M*	Φ_d
5.95	0	0.36
5.95	0.05	0.36
5.95	0.10	0.38

[a] In cyclohexane solution, the exciting wavelength was 343 nm.

Table V. Quantum Yields for the Phenanthrene-Sensitized Decomposition of **1a** at 270 nm in Cyclohexane

[**1a**], $M \times 10^4$	[Phenanthrene], $M \times 10^2$	[Piperylene], $M \times 10$	A,[a] %	Φ_d
12.9	2.50		99	0.21
8.21	1.01		98	0.26
8.21	1.01	1.0	98	0.25

[a] % of incident light absorbed by the sensitizer.

Since the luminescence experiments gave evidence only of the singlet state of the tetrazenes, attempts were made to quench the singlet state of **1a** by enhancing intersystem crossing. Concentrations of 0.05–0.1 *M* potassium iodide caused 10–30% quenching of the fluorescence of **1a** in ethanol, although no change in the luminescence spectrum indicative of phosphorescence was observed. Use of iodomethane as solvent failed also to lead to phosphorescence; in this case, changes in the extent of fluorescence could not be measured because the frozen solutions did not form clear glasses.

Discussion

Irradiation of each of the tetrazenes **1a–f** in the region of its long-wavelength absorption maximum caused smooth decomposition, principally to the corresponding *N*,*N*′-dimethylhydrazoarene (**2a–f**). The hydrazoarenes **2a** and **2c** have been shown to undergo photoreaction to give *N*-methylaniline and semidine products.[2,4] However, our control experiments with **2a**, as well as the presence of isosbestic points in the decomposition spectra of each of **1a–f**, indicate a single

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(10) G. Weber and F. W. J. Teale, *Trans. Faraday Soc.*, **53**, 646 (1957).

(11) P. S. Engel and P. D. Bartlett, *J. Amer. Chem. Soc.*, **92**, 5883 (1970).

phototransformation and the presence of only primary photoproducts.

We are now interested in understanding the nature of the primary photoprocesses. In contrast with hydrazoaromatics which both fluoresce and phosphoresce,[12] and with azo compounds which do neither,[13] we find that the tetrazenes **1a–f** fluoresce only. We have not been able to find evidence of a triplet state in **1a**, and all of our results indicate that the excitation chemistry of **1a** is confined to the singlet state. That is, traditional triplet quenchers and sensitizers of appropriate energy were able neither to quench nor to sensitize photodecomposition. In contrast, the singlet-sensitizer phenanthrene was able to sensitize photodecomposition of **1a** at a wavelength (270 nm) at which **1a** absorbs very weakly and under conditions in which essentially all of the incident light was absorbed by the phenanthrene. Phenanthrene has been shown to sensitize the decomposition of azo compounds,[11] a reaction which is known to occur in the excited-singlet state. By analogy, sensitization of the photodecomposition of **1a** by phenanthrene indicates that an excited singlet state of **1a** decomposes. Furthermore, the phenanthrene-sensitized decomposition was unaffected by the addition of the triplet-quencher piperylene, a test which has been used by Engel and Bartlett with azo compound photolyses to confirm singlet- rather than triplet-state involvement.

Our experiments with added potassium iodide and with solvent iodomethane also failed to engender phosphorescence of **1a**, although some reduction in fluorescence intensity was observed. Our results indicate that if **1a** achieves a triplet state this decays by a nonradiative path. We feel that the same will be true of other tetrazenes (**1b–f**), although we have not examined them in the same detail as **1a**.

Our luminescence experiments were carried out at 77°K whereas the photodecompositions were carried out at room temperature, at which solutions of the tetrazenes **1a–f** do not fluoresce. We assume, though, because we have direct evidence of an excited singlet state and none for a triplet state of **1a**, that the room-temperature photodecompositions also occur in the excited singlet state. With this in mind, we had anticipated that those tetrazenes which had the lower values of Φ_d would have the higher values of Φ_f. A situation somewhat similar to the one we anticipated has been reported, for example, by Kalmus and Hercules,[14] in connection with the photo-Fries rearrangement which occurs from an excited singlet state of an aryl ester.[15] That is, the relative fluorescence intensities of a number of phenol derivatives were the inverse of their so-called photo-Fries reactivities. However, our anticipation with the tetrazenes was not realized as is shown by Tables II and III. The results indicate that tetrazenes in excited singlet states have two pathways open to them. One of these pathways is either fluorescence (at 77°K) or decomposition (at room temperature). The other pathway is nonradiative decay, and we are unable to say whether this decay involves intersystem crossing or not. One would expect from the number of n–π^* and π–π^* states, which must surely be available in these aromatic tetrazenes, that intersystem crossing would be enhanced,[16] and, therefore, that any nonradiative decay would occur from a short-lived triplet rather than a singlet state. In such a case, the effect of para substituents on Φ_d would be tied to their effect on the efficiency of intersystem crossing. It does not seem that a more definitive description of substituent effects can be provided from our present data.

Nelsen and coworkers[9] have shown that photolysis of 1,4-di-*tert*-butyl-1,4-diaryl-2-tetrazenes gives radicals which belong to Walter's "S-class." Further, it has been shown that in the rates of thermal decomposition of tetrazenes such as **1a–f**, the effect of the aryl substituents is to control the ease with which the tetrazene acquires the appropriate conformation for decomposition.[17]

Similar detail in the photochemical decompositions of tetrazenes **1a–f** is not yet at hand. Circumstantial evidence for the involvement of *N*-methylanilino radicals in the formation of **2a** at low temperature was obtained, however, in an interesting way. Irradiation of **1a** at 77°K gave the usual fluorescence spectrum of **1a**. Irradiation for a prolonged period was unaccompanied by phosphorescence, but when the ethanol glass was allowed to thaw and was refrozen and reirradiated the phosphorescence spectrum of **2a** was obtained. That is, it seems that *N*-methylanilino radicals were formed at 77°K and recombined to **2a** when the glass was warmed.

The overall view of photodecomposition of a tetrazene (**1a–f**) at room temperature is that an excited-singlet reaction occurs and the major product is the hydrazo compound. A rearrangement product (*e.g.*, **3**) is also likely to be formed in the initial photoprocess. Radicals may be involved in both types of recombination reactions (*e.g.*, to give **2a** and **3**), but direct evidence of radicals has not been obtained.

Experimental Section

Preparation of Tetrazenes 1a–f. Tetrazenes **1a–f** were prepared according to the methods of Nelsen and Heath.[17]

Quantum Yields. Solutions of tetrazenes **1a–f** in cyclohexane (Eastman Kodak Spectroquality) or methanol were prepared and deoxygenated by nitrogen bubbling. Samples of 3.00 ml of the solutions in cuvettes were irradiated using a Bausch and Lomb Model 33-86-07 monochromator set for a 10-nm bandwidth and the 340–380-nm absorption maximum of the tetrazene under study. The extent of photodecomposition was monitored at regular intervals using a Cary 14 uv spectrophotometer. Concentrations were chosen so that the tetrazene absorbed a minimum of 90% of the incident light, and the results were corrected for the actual absorption. Incident light intensity was measured both before and after each irradiation using the potassium ferrioxalate actinometer of Hatchard and Parker.[18] Quantum yields were calculated from the extent of tetrazene disappearance in the spectrum, and at conversions of less than 10%. Results are given in Table II.

Isosbestic Points. Solutions of tetrazenes **1a–f** were irradiated and monitored as for quantum yield decomposition, except that irradiation was continued until the uv spectra indicated complete decomposition of the tetrazenes. In each case, one or more isos-

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(12) C. M. Baldwin, P.-S. Song, and H. J. Shine, *J. Amer. Chem. Soc.*, **92**, 3284 (1970).

(13) R. N. Nurmukhamentov, D. N. Shigorin, Yu. L. Kozlov, and V. A. Puchkov, *Opt. Spectrosc.*, **11**, 327 (1961).

(14) C. E. Kalmus and D. M. Hercules, *Tetrahedron Lett.*, 1575 (1972).

(15) (a) J. W. Meyer and G. S. Hammond, *J. Amer. Chem. Soc.*, **94**, 2219 (1972); (b) M. R. Sandner, E. Hedaya, and D. J. Trecker, *ibid.*, **90**, 7249 (1968).

(16) M. A. El-Sayed, *Accounts Chem. Res.*, **1**, 8 (1968).

(17) S. F. Nelsen and D. H. Heath, *J. Amer. Chem. Soc.*, **91**, 6452 (1969).

(18) C. G. Hatchard and C. A. Parker, *Proc. Royal Soc., Ser. A*, **235**, 518 (1956).

bestic points were observed, indicating the photolysis of only a single species.

Photolysis of 1c. Tetrazene **1c** (93.3 mg, 0.35 mmol) was dissolved in 200 ml of Spectroquality cyclohexane in a Pyrex tube, and the solution was deoxygenated by nitrogen bubbling. Irradiation was carried out with the Bausch and Lomb monochromator at 345 nm using a 45-nm bandpass, and was monitored by the periodic uv analysis of aliquots. Complete tetrazene decomposition required 2 hr. The concentrated photolysate was chromatographed on a 20 × 20 cm tlc plate of 10 g of Brinkmann silica gel GF_{254} developed with benzene. The major band, R_f 0.6, was removed from the plate and extracted with benzene to yield 72.3 mg (0.29 mmol, 83%) of *N*,*N'*,4,4'-tetramethylhydrazobenzene, identified by comparison of its nmr spectrum with that of an authentic sample: nmr (CCl_4) δ 2.20 (s, 6 H, $ArCH_3$), 2.82 (s, 6 H, NCH_3), 6.56 and 6.87 (pseudo AB q, $J = 9$ Hz, 8 H, arom).

Photolysis of 1d. Tetrazene **1d** (55.4 mg, 0.182 mmol) was irradiated as described above at 350 nm for 18 hr. The major chromatography band, R_f 0.6, was removed from the plate and extracted with benzene to yield 29.3 mg (0.104 mmol, 57%) of *N*,*N'*-dimethyl-4,4'-dichlorohydrazobenzene, mp 71–73°, identified by comparison with an authentic sample: nmr ($CDCl_3$) δ 2.94 (s, 6 H, NCH_3), 6.72 and 7.18 (pseudo AB q, $J = 9$ Hz, 8 H, arom).

Photolysis of 1f. Tetrazene **1f** (50 mg, 0.13 mmol) was similarly irradiated at 380 nm for 4 hr. The photolysate was chromatographed on a tlc plate, 20 × 20 cm, of 10 g of Brinkmann silica gel GF_{254}, developed with 10% ethanol–benzene. The major band, R_f 0.7, was removed from the plate with benzene and shown by nmr to contain 29 mg (0.11 mmol, 83%) of *N*,*N'*-dimethyl-4,4'-dicarbethoxyhydrazobenzene, identified by comparison with an independently prepared sample (*vide infra*). The product also contained traces of another photoproduct of the tetrazene, which was not identified.

Preparation of Ethyl *p*-Nitrosobenzoate. The preparation followed the general procedure of Havinga and coworkers.[19] Ethyl *p*-nitrobenzoate (30.5 g, 0.15 mol) was dissolved in 125 ml of ethanol, 50 ml of methyl cellosolve, and 12 ml of water. Ammonium chloride (2.3 g) was added and the solution was heated to boiling. Powdered zinc (18 g, 0.36 mol) was added slowly, maintaining a gentle reflux, over 20 min. The mixture was filtered and the filtrate, containing the hydroxyamine, was oxidized by pouring into an ice-cold solution of ferric chloride (23 g, 0.085 mol) in 600 ml of water. A yellow precipitate formed which was collected by filtration to yield 24.0 g (0.13 mol, 86%) of ethyl *p*-nitrosobenzoate, visible spectrum λ_{max} (CH_2Cl_2) 770 nm.

Preparation of 4,4'-Dicarbethoxyazobenzene. The compound was prepared following the general method of Gatterman and Wieland.[20] Ethyl *p*-nitrosobenzoate (24 g, 0.13 mol) and ethyl *p*-aminobenzoate (16.5 g, 0.1 mol) were dissolved in 100 ml of ethanol and 30 ml of glacial acetic acid. The solution was warmed gently for 30 min, then 10 ml of water was added and the solution was cooled. Orange needles formed and were collected by filtration to yield 9.3 g (0.026 mol, 20%) of 4,4'-dicarbethoxyazobenzene: mp 142–144°; nmr ($CDCl_3$) δ 1.45 (t, $J = 7$ Hz, 6 H), 6.98 and 7.32 (pseudo AB q, $J = 9$ Hz, 8 H, arom).

Preparation of 4,4'-Dicarbethoxyhydrazobenzene. 4,4'-Dicarbethoxyazobenzene (2.0 g, 5.6 mmol) was dissolved in 50 ml of benzene and 10 ml of ethanol. Powdered zinc (5 g, 0.08 mol) was added and the mixture was stirred overnight. The mixture was filtered and concentrated to allow the formation of colorless crystals. These were collected by filtration to yield 0.93 g (2.8 mmol, 50%) of 4,4'-dicarbethoxyhydrazobenzene: mp 122–124°; nmr ($CDCl_3$) δ 1.36 (t, $J = 7$ Hz, 6 H), 4.35 (q, $J = 7$ Hz, 4 H), 6.12 (s, 2 H, NH), 6.80 and 7.92 (pseudo AB q, $J = 9$ Hz, 8 H, arom).

Preparation of *N*,*N'*-Dimethyl-4,4'-dicarbethoxyhydrazobenzene. 4,4'-Dicarbethoxyhydrazobenzene (0.88 g, 2.7 mmol) was dissolved in 100 ml of tetrahydrofuran and stirred under nitrogen. Sodium hydride (127 mg, 57% in mineral oil, 2.7 mmol) was added and the solution was stirred 5 hr until a dark color had formed. Iodomethane (252 mg, 2.7 mmol) was added and the solution stirred 1 hr. Addition of sodium hydride and iodomethane was repeated as before. The solution was poured into 100 ml of benzene and washed three times with water, dried, and concentrated to yield 1.09 g of *N*,*N'*-dimethyl-4,4'-dicarbethoxyhydrazobenzene as a colorless oil contaminated with mineral oil: nmr ($CDCl_3$) δ 1.37 (t, $J = 7$ Hz, 6 H), 3.13 (s, 6 H, NCH_3), 4.34 (q, $J = 7$ Hz, 4 H), 6.76 and 7.96 (pseudo AB q, $J = 8$ Hz, 8 H, arom).

Control Photolysis of *N*,*N'*-Dimethylhydrazobenzene. Separate solutions of **1a** (5.50×10^{-5} *M*) and *N*,*N'*-dimethylhydrazobenzene (3.87×10^{-5} *M*) in cyclohexane in 3-ml cuvettes were each irradiated 1 hr using the Bausch and Lomb monochromator at the same wavelength (343 nm) and slit widths. At the end of the photolysis the uv spectra showed tetrazene **1a** to be 90% decomposed, while no change was observable in the *N*,*N'*-dimethylhydrazobenzene. The solutions were concentrated and chromatographed side by side on an Eastman Kodak Chromagram silica gel plate developed with benzene. Three products were visible from **1a**: *N*,*N'*-dimethylhydrazobenzene (R_f 0.55), *N*-methylaniline (0.25), and *p*-semidine (**3**) (0.07). The *N*,*N'*-dimethylhydrazobenzene photolysis solution showed only starting material.

Acetone-Sensitized Photolysis of 1a. A solution of **1a** in 1:1 acetone–cyclohexane was prepared and irradiated as described above for quantum yield determinations. Irradiation was at 270 nm, where the acetone was calculated to absorb 99.8% of the incident light. The acetone did not interfere with the observation of the 343-nm peak of the tetrazene. After 1 hr irradiation, and using potassium ferrioxalate actinometry,[18] the quantum yield of photodecomposition of **1a** was calculated to be 0.012, about 3% of the value for direct irradiation.

Oxygen-Quenched Photolysis of 1a. Duplicate solutions of **1a** in cyclohexane were prepared. One solution was carefully degassed by the freeze–thaw technique while the second received no degassing. Irradiation as described above for quantum yield determinations showed no difference in the quantum yield of photodecomposition for the two solutions.

Quenching by Piperylene of the Photolysis of 1a. Separate solutions of **1a** in cyclohexane containing 0.05 and 0.10 *M trans*-piperylene were prepared as described above for quantum yield determinations and irradiated at 343 nm using the Bausch and Lomb monochromator. Incident light intensity was measured using potassium ferrioxalate actinometry.[18] Quantum yields for photodecomposition are given in Table IV.

Phenanthrene-Sensitized Photolysis of 1a. Solutions of tetrazene **1a** and phenanthrene in cyclohexane (with or without added piperylene) were prepared and irradiated as described above for quantum yield determinations. Irradiation was at 270 nm, where phenanthrene was calculated to absorb about 99% of the light in all cases. The solutions were diluted for uv analysis. The phenanthrene did not interfere with monitoring the 343-nm peak of **1a**. Potassium ferrioxalate actinometry was used to determine the incident light intensity,[18] and quantum yields for the photodecomposition of **1a** were calculated at less than 10% conversion. Results are given in Table V. Phenanthrene was determined to be stable under the conditions of the photolysis.

Luminescence Studies. Luminescence spectra were recorded on an Aminco-Bowman spectrophotofluorometer which could be equipped with a phosphoroscope when desired. Solutions of the tetrazenes were prepared in Spectroquality absolute ethanol and deoxygenated by nitrogen bubbling. Uv absorbances of the solutions were measured in 1-cm cells, and the luminescence spectra were recorded with the use of 3-mm quartz tubes at 77°K. For quantitative measurements, solutions of each of **1b–f** were compared against **1a** using the same excitation wavelength and slit widths. Sample absorbances were kept very low (0.1–0.2) and the results were corrected for the actual absorbances at the exciting wavelength. Relative fluorescence intensities were measured by cutting and weighing the emission bands from the chart paper. As a measure of the absolute fluorescence quantum yield, **1a** was compared against anthracene (which absorbs and emits at similar wavelengths to **1a**). Anthracene fluorescence was determined at room temperature and assigned a value of Φ_f of 0.30.[10] Tetrazenes **1a–f** showed no luminescence at room temperature. Results are given in Table III.

Fluorescence Quenching. Solutions of **1a** were prepared as above in ethanol containing 0.1 *M* potassium iodide and a trace of water to enhance solubility. In several trials, decreases of 10–30% in the fluorescence intensities were observed as compared with control solutions containing no potassium iodide. No change in the spectra indicative of phosphorescence enhancement was observed with or without the phosphoroscope. Under similar conditions anthracene showed comparable fluorescence quenching accompanied by a clear increase in phosphorescence.

Fluorescence in Iodomethane. A solution of **1a** in iodomethane was prepared and its luminescence spectrum recorded as above. The spectrum had the same maximum and shape as that measured

(19) W. J. Mijs, S. E. Hoekstra, R. M. Ulmann, and E. Havinga, *Recl. Trav. Chim. Pays-Bas*, 77, 746 (1958).

(20) L. Gatterman and H. Wieland, "Laboratory Methods of Organic Chemistry," Macmillan, New York, N. Y., 1937, p 181.

in ethanol. The intensity could not be measured since a clear glass could not be obtained.

Photolysis of 1a at 77°K. A solution of **1a** in ethanol was prepared and its fluorescence spectrum measured as described above. Use of the phosphoroscope showed no phosphorescence from the solution. The solution, maintained at 77°K, was irradiated for 15 min using 345-nm light from the Bausch and Lomb monochromator. Remeasurement of the luminescence spectra showed a decrease in the fluorescence intensity but no phosphorescence. The glass was allowed to thaw and was then refrozen. Use of the phosphoroscope now showed the phosphorescence spectrum of **2a**.[12]

The Deamination of Bridgehead Amines *via* the Nitroso- and Nitroamide Approach[1]

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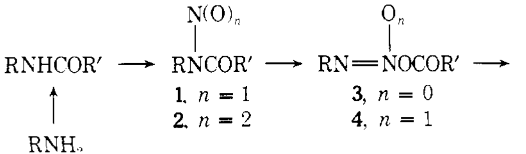
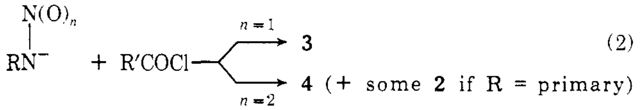
Abstract: 1-Norbornylamine, 1-apocamphylamine, and 1-adamantylamine have been deaminated using the nitroso- and nitroamide approach. The reaction yields carbonium ions that are reactive enough to abstract chloride ions from solvents such as methylene chloride, probably *via* chloronium ion species. The norbornyl ions have a much higher reactivity than the 1-adamantyl ions as shown by the higher ratio of solvent attack to reaction with the negatively charged counterion. Oxygen-18 tracer experiments are also reported. The mechanism of deamination is discussed based on these and other results.

The deamination of aliphatic amines *via* the nitroso- and nitroamide approach (eq 1) is a useful variant



$$\underset{\underset{\mathrm{RNH_2}}{\uparrow}}{\mathrm{RNHCOR'}} \longrightarrow \underset{\mathbf{1},\ n=1;\ \mathbf{2},\ n=2}{\overset{\mathrm{N(O)}_n}{\overset{|}{\mathrm{RNCOR'}}}} \longrightarrow \underset{\mathbf{3},\ n=0;\ \mathbf{4},\ n=1}{\mathrm{RN{=}\overset{O_n}{\overset{|}{N}}OCOR'}} \longrightarrow \mathrm{RO_2CR'} + \mathrm{N_2(or\ N_2O)} \qquad (1)$$

of the older nitrous acid method, because of the wider range of temperatures and solvents that can be used and because of the greater control over the counterion ($R'CO_2^-$) that is possible.[2] An alternative synthesis of the reaction intermediates **3** and **4** *via* the "salt" approach (eq 2) adds to the versatility of the method.[3,4]



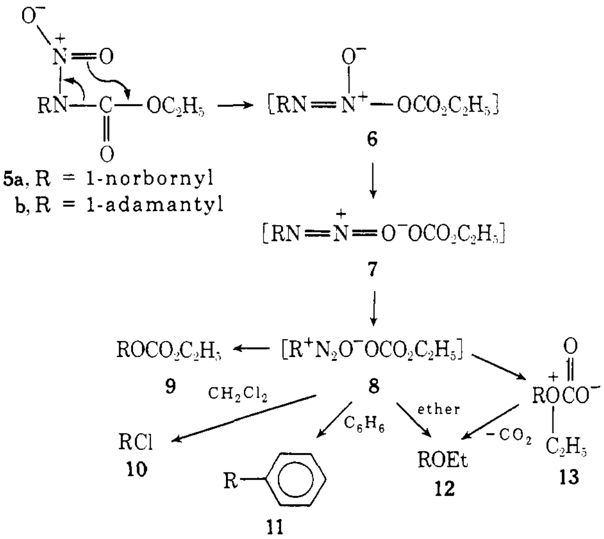
$$\overset{\mathrm{N(O)}_n}{\overset{|}{\mathrm{RN^-}}} + \mathrm{R'COCl} \begin{cases} \xrightarrow{n=1} \mathbf{3} \\ \xrightarrow[n=2]{} \mathbf{4}\ (+\text{ some } \mathbf{2} \text{ if R = primary}) \end{cases} \qquad (2)$$

These reactions yield carbonium ions (R^+) and, typically, they not only yield esters (eq 1) but also olefins. For branched R groups the ester yields can be low, largely because of the predominance of the elimination pathway. To avoid olefin formation and also to gauge the effect of enhanced carbonium ion reactivity, we have examined the deamination of bridgehead systems.[5,6] This paper covers work on the deamination of 1-norbornylamine, 1-apocamphylamine, and 1-adamantylamine; the results reveal an extraordinarily high reactivity for the carbonium ions formed.

Procedure and Results

Nitration of ethyl *N*-1-norbornyl- and *N*-1-adamantylcarbamates with fuming nitric acid afforded *N*-nitrocarbamates **5a** and **5b** (Scheme I).[7,8] The *N*-nitrocarbamates were decomposed at 50 and 105° to yield nitrous oxide, the corresponding carbonates, and products derived from reactions with the solvents. The products were identified by their glpc retention times and by isolation and proof of structure through spectral and analytical means. The results for the

Scheme I



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(1) Some of the results described in this paper have appeared in preliminary form: E. H. White, H. P. Tiwari, and M. J. Todd, *J. Amer. Chem. Soc.*, **90**, 4734 (1968).

(2) E. H. White and D. J. Woodcock in "The Chemistry of the Amino Group," S. Patai, Ed., Wiley, New York, N. Y., 1968.

(3) (a) E. H. White and D. W. Grisley, Jr., *J. Amer. Chem. Soc.*, **83**, 1191 (1961); (b) R. A. Moss and K. M. Luchter, *J. Org. Chem.*, **37**, 1155 (1972).

(4) E. H. White, T. J. Ryan, and K. W. Field, *J. Amer. Chem. Soc.*, **94**, 1360 (1972).

(5) P. D. Bartlett and L. H. Knox (*ibid.*, **61**, 3184 (1939)] reported on the reaction of 1-apocamphylamine with nitrous acid and nitrosyl chloride.

(6) For a review of bridgehead reactivity and bridgehead cations *via* deamination, see R. C. Fort, Jr., and P. v. R. Schleyer, *Advan. Alicyclic Chem.*, **1**, 283 (1966).

(7) E. H. White, M. C. Chen, and L. A. Dolak, *J. Org. Chem.*, **31**, 3038 (1966).

(8) The ir spectra of **5a** and **5b** show two carbonyl peaks. For **5a** these peaks appear at 1750 and 1775 cm^{-1}, and for **5b** at 1738 and 1765 cm^{-1}. As previously noted,[7] these bands are assigned to two rotamers formed by rotation about the amide linkage.

White, et al. / Deamination via the Nitroso- and Nitroamide Approach